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The Application of General MOS Gas Sensors for Discriminating Formalin Content

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Abstract

This paper describes the application of Metal Oxide Semiconductor (MOS) gas sensors which are intrinsically designed to sense volatile compounds for measuring the vapor of formalin. We utilized 7 commercial MOS gas sensors (namely TGS-2600, TGS-2602, TGS-2620, TGS-813, MQ-137, MQ-135, and MQ-5) to sense formalin in certain concentrations and their presence in meat. We built a static headspace system to measure the vapor of formalin. The sensor chamber is 540-cm^3, made from 5 mm acrylic. The output of MOS (Sensitivity ratio) is acquired into computer using an Arduino-based interface. We tested 3 concentrations of formalin (10%, 20% and 30%) and their presence in meat. We found that individually each sensor provides proportional response to formalin concentrations, and for their presence in meat as well. The Principle Component Analysis (PCA) method is used to show performance of the array MOS sensor in discriminating the formalin contents. The PCA result shows that by using two PCs (holding most 96% data), it can clearly distinguish the three formalin contents. However the array sensors just can discriminate clearly between meat containing formalin and those not. The success rate of discrimination the formalin contents in meat is 91.7%.

Keywords*: MOS gas sensor, formalin, volatile compound, vapor measurement, PCA*

1. Introduction

The abuse of formalin usage as in Indonesia still makes much threat to public society. It is still found many abuses in small food industries [1, 2] and traditional markets [3]. The techniques to know the presence of formalin had been many investigated [4–7]. The most sensitive and accurate is laboratory-based spectroscopy by using methods of ultra violet (UV) spectrophotometer, high performance liquid chromatography (HPLC), and Gas Chromatography (GC) [4]. However, those methods require long time, high skill, many reagents, and high cost. A special reagent, namely Schiff reagent, had been succefully tested to indicate the formalin in food [5]. One low cost-alternative method to indicate the formalin is by using turmeric solution [6, 7]. Yet, the reagent and turmeric require careful reading of indicator. They only indicate positive or negative formalin by its changed-color reading. Moreover, it cannot be used repeatedly (only once usage). Hence it is needed other approaches which able to indicate the formalin content easily, quickly, and accurately.

Formalin or formaldehyde chemical compound, is a gas-shaped aldehyde with the chemical formula H_2CO. Formalin is a colorless solution, flammable, corrosive, sharp odor and volatile, containing about 37% to 50% formaldehyde in water [8]. Based on those properties of formalin, it is possible to indicate presence and estimate the formalin content by sensing the vapor using gas sensors, which capture the volatile compounds, emitted from formalin or substance containing formalin. The growth in material technology has leaded much substance that can be used as volatile sensor material, such as polymer and metal oxide semiconductor. Gunawan and Sudarmaji [9] has used some composites of polymer-carbon (such as Polyethylene Glycol (PEG)-6000, PEG-1540, PEG-20M, and PEG-200) to measure and indicate the formalin in several foods by using the principle of electronic nose technology with artificial neural network as

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pattern recognition tool. But for wide applications, those polimer-carbon composites are not simple to be made and their availability are not many yet.

One material that has been produced widely by many manufacture is Metal Oxide Semiconductor (MOS), i.e. SnO_2 semiconductor gas sensor. Various types of MOS gas sensor have been fabricated to measure the compounds of air pollutant gases, such as carbon monoxide, hydrocarbons, nitro oxide, volatile organic compound, and others [10]. Sa'diyah *et al* [11] employed two MOS gas sensors to detect the liquid of formalidehide. Since the specific MOS gas sensor for formalin detection is not available yet, therefore the use of array MOS gas sensor is suitable for detecting the volatile gases from formaldehyde. This approach is like design of mammalian olfactory system, in which does not use the single specific sensor. Instead, a sensor series comprising a number of sensor elements with each sensor element responding to a certain amount of vapor. The response of a partially sensor element may overlap with other sensor element responses. Although in this approach the process of identifying a vapor cannot be achieved by a single sensor element, yet the series of sensors will generate and form a unique pattern/profile for each type of vapor. The array of sensors can identify complex vapors without requiring the breakdown of their constituent components first during the analysis.

This paper presents our preliminary work in usage of array MOS gas sensor that intrinsically designed to sense general volatile compounds for measuring and discriminating the vapor of formalin and food containing formalin. The Regression and Principle Component Analysis (PCA) method are used to show the performance of individual sensor and array MOS sensor in discriminating the formalin contents respectively.

2. Research Method

2.1. Experimental Design

This experimental research was conducted at Laboratory of Agricultural Engineering, Jenderal Soedirman University from July 2017 to December 2017. We built a measurement system by using method of static headspace to measure the vapor of formalin. The design of vapor measurement of formalin is shown in Figure 1. Seven MOS gas sensors (i.e. TGS-2620, TGS-2600, TGS-2602, TGS-813, MQ-5, MQ-135, and MQ-137) are utilized which placed in a sensor chamber by size 540 cm^3 square box, made from 5 mm acrylic. The output of MOS is acquired into a PC using an Arduino-based interface.

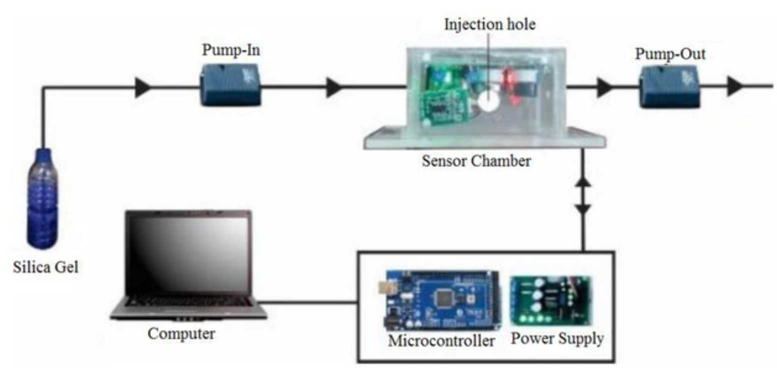

Figure 1. Measurement diagram of formalin vapor using MOS gas sensors

2.2. Formalin Sample Preparation

We use the formalin type of Pro Analysis (PA) to prepare samples of formalin, which contains 37%, 200 ml. We made a dilution by adding distilled water into the PA to get the desired concentration of formalin. The volume of distilled water is determined using (1). We tested three concentrations of formalin (10%, 20%, and 30%). Table 1 shows the addition of distilled water into the PA to obtain certain concentration of formalin.

$$V_1 x\, M_1 = (V_1 - V_2)\, x\, M_2 \quad (1)$$

where,
V_1= volume of PA (200 ml),
M_1= concentration of PA (37%),
V_2= volume of distilled water addition (ml), and
M_2= concentration of desired formalin concentration (%).

Table 1. Addition of Distilled Water into the PA Formalin (37% 200 ml).

Desired formalin content	Addition of distilled water into The PA formalin
10 %	540 ml
20 %	170 ml
30 %	46.67 ml

Then the three formalin concentrations are separated into two sample groups, formalin solution and meat containing each formalin concentration. A sample of formalin solution is 1 ml and placed inside the rubber-capped vial. While a sample of meat containing formalin is 2 g and placed inside the 100 ml rubber-capped vial. Figure 2 shows example of the prepared samples and the injection process of samples.

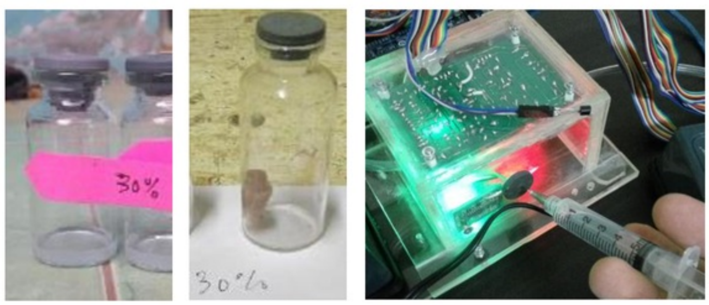

Figure 2. (a) Sample of 30% formalin, (b) sample of meat containing 30% formalin, and (c) injection of sample vapor into sensor chamber.

2.3. Measurement steps

There are 3 steps in measuring vapor of formalin with static headspace system either for the formalin solution or for formalin content in meat. They are Idle (Cleaning), Baseline Measurement (R_O), and Formalin Measurement (R_S). The Idle and R_O are when the sensors are not measuring the vapor of formalin. The flow is set from the silica gel container to sensor chamber and then to out by turning on the Pump-In and Pump-Out. While The R_S (measuring the formalin) is by injecting the vapor into sensor chamber from injection hole, the Pump-In and Pump-Out are turned off. One cycle measurement of formalin sample, shown in Figure 3, consists of acquiring R_O for 1 minute, and then injects the formalin vapor from sample vial into sensor chamber using 5 ml syringe and followed by R_S for 1 minute. After that the purging of sensor chamber is done in 5 minutes. Each measurement of formalin sample is repeated 5 times.

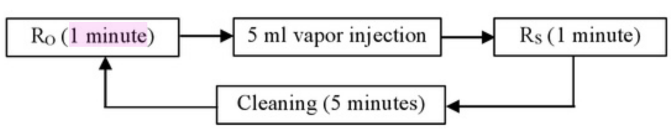

Figure 3. Measurement diagram of formalin vapor.

The output of MOS gas sensors are represented by Sensitivity ratio (S) as R_O / R_S, where R_O is Resistance of MOS gas sensor when measuring the dry air and R_S is Resistance of MOS gas sensor when measuring the vapor of formalin. And the response of individual MOS gas sensor and performance of array MOS gas sensor are expressed by method of regression and PCA respectively.

In our investigations, we examined the MOS gas sensors to:

a. Discriminate three concentrations of formalin solution: 10 %, 20 %, and 30%.
b. Discriminate four formalin content in meat: contained 0%, contained 10%, contained 20%, and contained 30 %.

3. Results and Analysis

3.1. The Prototype of Volatile Measurement System using MOS Gas Sensors

Figure 4 shows the prototype of formalin vapor measurement system based on MOS gas sensors. It mainly consists of array MOS gas sensor inside sensor chamber, Arduino Mega2560-based interface, static headspace with vapor transport system, and acquisition software.

(a) (b)

Figure 4. (a) Prototype and (b) acquisition software of the formalin vapor measurement.

3.2. Individual Response of MOS Gas Sensor to Formalin Vapor

Response (S) of each MOS gas sensor when sensing the vapor of formalin solution and meat exposed with formalin are shown in Figure 5 and Figure 6 respectively. A linear regression is applied to show the linearity and correlation between sensor output and concentration of formalin as shown in Table 2.

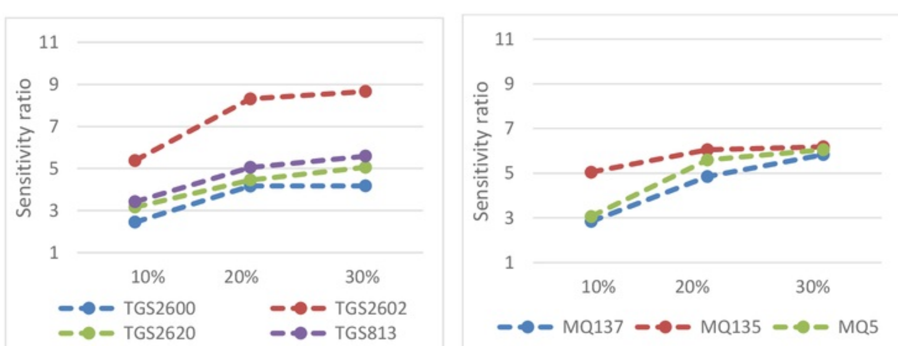

Figure 5. Response (S) MOS gas sensors to vapor of formalin on 10%, 20%, and 30%.

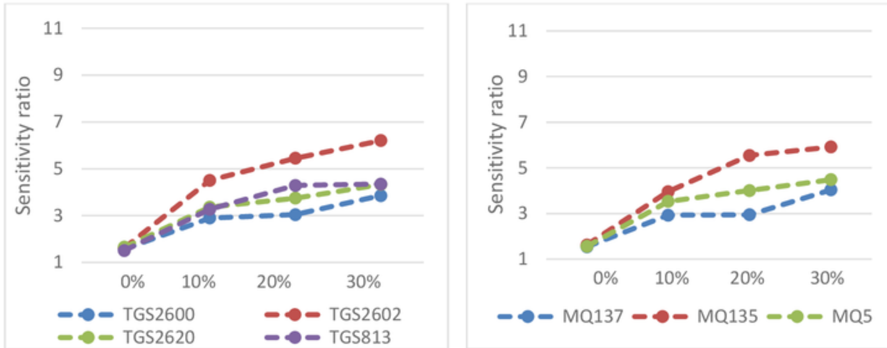

Figure 6. Response (S) MOS gas sensors to meat containing 10%, 20%, and 30% formalin.

Table 2. Equation of Linear Regression of MOS Gas Sensors to Formalin Solution.

Sensor	Linear Regression	R^2
TGS-2600	y = 0.862x + 1.871	0.754
TGS-2602	y = 1.644x + 4.166	0.829
TGS-2620	y = 0.948x + 2.331	0.958
TGS-813	y = 1.086x + 2.514	0.921
MQ-5	y = 1.490x + 1.923	0.862
MQ-135	y = 0.569x + 4.622	0.837
MQ-137	y = 1.496x + 1.518	0.963

As shown in Figure 5 and Figure 6, it is clearly seem that all sensor able to sense the vapor of formalin and its presence in meat. The response is proportional to the concentration of formalin, the higher content of formalin leads higher Sensitivity ratio. Yet the linearity is not really strong. It indicates that high concentration of formalin will provide more volatile compounds, thus the resistance of sensor is decrease proportionally to the formalin content. It is also shown that TGS-2602 and MQ-137 provide most linear and high sensitivity to content of formalin solution and the meat containing formalin. They have highest slope coefficient and determination coefficient (R^2), i.e. respectively 1.644 and 0.829 for TGS-2602, and 1.496 and 0.963 for MQ-137. The slope defines the sensor sensitivity to the change of vapor of formalin sample. The higher slope means the higher sensitivity of sensor to discriminate the content of formalin. And determination coefficient explains the model (equation) in determining the change in dependent variable.

However, we also found that there is still cross sensitive from 5 repeats measurement of each sample, especially when discriminating the meat containing formalin either between 10% and 20% or between 20% and 30%. For example, as shown in Figure 5, the slope of Sensitivity ratio between TGS-2600 and MQ-135 to formalin solution 20% and 30% are not high. Their values are nearly the same.

3.3. PCA Loading Plot for Determining Individual Response of MOS Gas Sensors

Principle Component Analysis (PCA) allows simplifying a data by transforming linearly into new dimension with maximum variants. The new dimension consists of Principal Components (PCs) which in accordance with the number of sensors / variables used. Hence, a PC is data covariant of whole sensors. And, the loading plot of PCA describes all sensor responses. It is expressed by straight line corresponding the amount of sensors. Every lines are centered at a point, and the length of line explains the how strong the sensor (variable) contributes to the samples measured [12]. Figure 7 and Figure 8 show the loading plot of MOS gas sensors in measuring the formalin solution and meat exposed by formalin respectively. It clearly seem that all MOS gas sensor have almost same significant contribution to PC1 and PC2. The length of seven MOS gas sensor is quit similar.

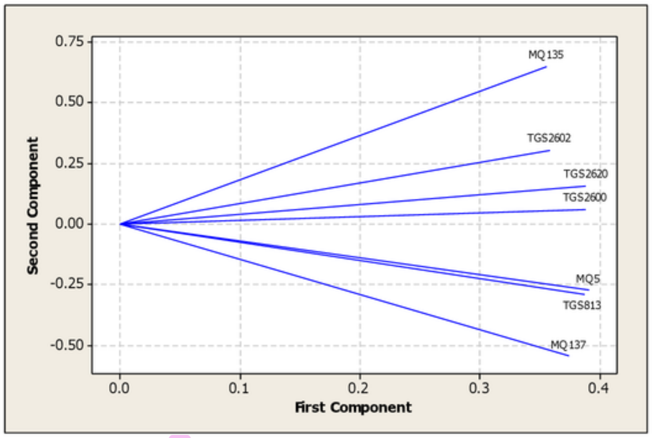

Figure 7. Loading Plot of array MOS gas sensor to vapor of formalin solution.

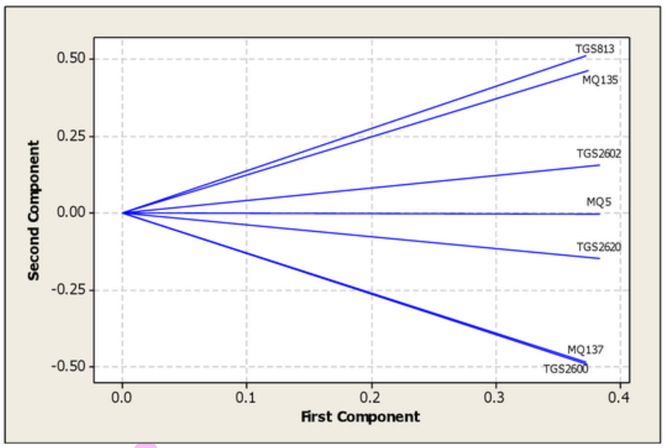

Figure 8. Loading Plot of array MOS gas sensor to vapor of meat containing formalin.

3.4. Identification of Formalin Content by Means of PCA

We used the PCA to examine the identification performance of array of 7 MOS in discriminating the content of formalin solution and formalin presence in meat. PCA is commonly used as feature extraction to test distinguish performance and a powerful linear classification technique and visualization the difference in similarities or differences among the treatments.

PCA is also many used as feature extraction in term of Electronic-nose technology. Electronic-nose technology had been successfully and widely applied in the authentication of a wide range of food types [13]. Zhang et al [14] used six TGS gas sensors for spoiling and formaldehyde-containing detection in an octopus by using PCA technique. Fresh octopus samples is dipped in water solutions with different formaldehyde concentration. The results show that electronic nose analysis could be an efficient method for seafood quality assessment; the spoilage of seafood could be easily detected.

Respectively Figure 9 and Figure 10 show the plot of 2 PCs in discriminating the three formalin solutions and their presence in meat. It clearly seen that the first two principal component could represent the output of seven MOS gas sensor used, cumulatively they hold more than 96% of data. Typically, the first two or three uncorrelated PCs hold most significant of variation present in all variables and widely used in various application [15].

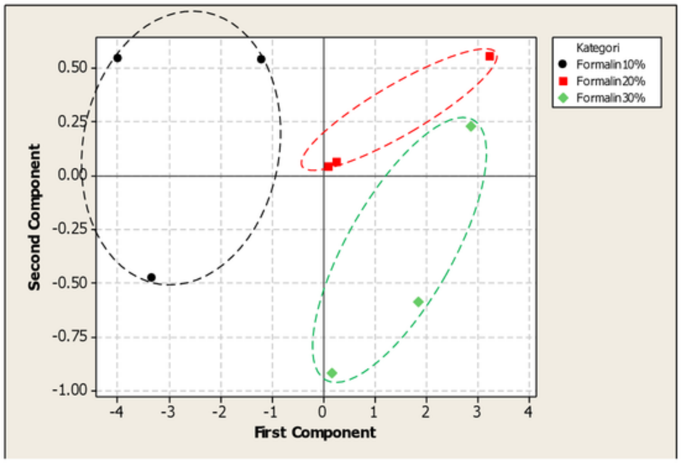

Figure 9. Plot of 2 PCs in discrimination among formalin solution 10%, 20% and 30%.

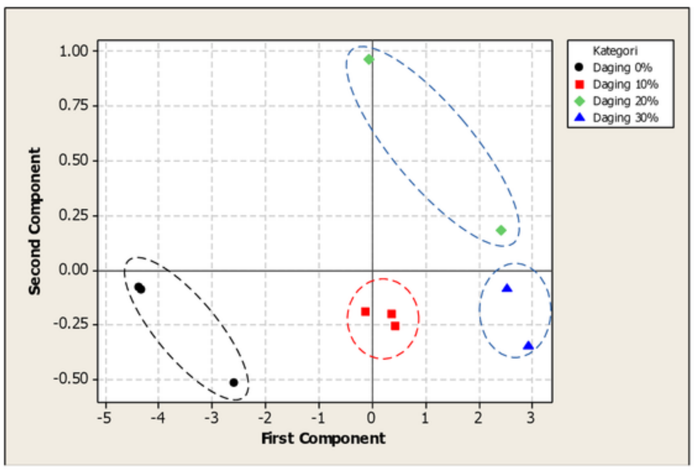

Figure 10. Plot of 2 PCs in discrimination among meat dipped into formalin solution 0%, 10%, 20% and 30%.

In Figure 9, it is seen that the system is able to discriminate fairly among 10% formalin, 20% formalin, and 30% formalin. There is not a miss-classification in each group and the distance among their averages is far. And the system also can distinguish clearly between meat without formalin and meat containing formalin (Figure 10). The distance between meat without formalin (0%) and meat containing formalin (10%, 20%, and 30%) is separated clearly. Yet, as shown in Figure 10, there is a coordinate of meat with 20% formalin, which close to group of meat with 30% formalin. It may lead miss discrimination between them. The success rate of discrimination the formalin content in meat is 91.7%. Zhang *et al* [14] who use the PCA to recognize the octopus that containing formalin, the recognition rate of different octopus samples was 93.1%. Another work, Sa'diyah *et al* [11] employed TGS-2600 and TGS-2611 to build a device to detect the liquid and solid formalin of three concentrations (5 ppm, 10 ppm, and 20 ppm), in which the success rate was about 97%. Their device is not tested to formalin contained in a food yet.

4. Conclusion

In this paper, we present a work of use of seven MOS gas sensors, which intrinsically designed sensitive to volatile compounds to measure the vapor of formalin and its presence in meat. The MOS gas sensors are TGS-2600, TGS-2602, TGS-2620, TGS-813, MQ-137, MQ-135, and MQ-5. We tested formalin solution of Pro Analysis in three concentration (10%, 20%, and 30%) and meat which dipped into those formalin solutions. We examined the discrimination performance of MOS gas sensors both individual and in array. We found that the response of each MOS gas sensor is proportional to content of formalin and provides relatively the same contribution to distinguish the formalin. Moreover we found TGS-2602 and MQ-137 provide most linear and highest sensitivity to content of formalin solution and the meat containing formalin. Using PCA, the seven MOS gas sensors are able to discriminate clearly the three formalin solution and to indicate the meat whether containing formalin or not as well. However, there is potential miss discrimination when indicating between the meat with 20% formalin and meat with 30% formalin. The success rate of discrimination the formalin contents in meat is 91.7%.

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